

10/565253

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Fungicidally active compound combinations

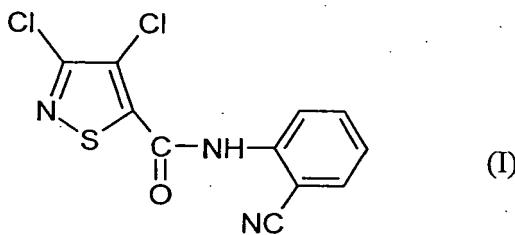
The present invention relates to novel active compound combinations which comprise the known 2'-cyano-3,4-dichloroisothiazole-5-carboxanilide on the one hand and other known fungicidally active compounds on the other hand, and which are highly suitable for controlling phytopathogenic fungi.

It is already known that 2'-cyano-3,4-dichloroisothiazole-5-carboxanilide has fungicidal properties (cf. WO 99-024 413). The activity of this substance is good; however, at low application rates it is in some cases unsatisfactory.

Furthermore, it is already known that numerous triazole derivatives, strobilurins, aniline derivatives, carboxamides and various heterocycles can be used for controlling fungi (cf. EP-A 0 040 345, DE-A 2 234 010, EP-A 0 382 375, EP-A 0 515 901 and Pesticide Manual, 9th. Edition (1991), pages 391, 506, 746 and 846). However, the activity of these substances at low application rates is likewise not always sufficient.

It has now been found that the novel active compound combinations consisting of 20

2'-cyano-3,4-dichloroisothiazole-5-carboxanilide of the formula



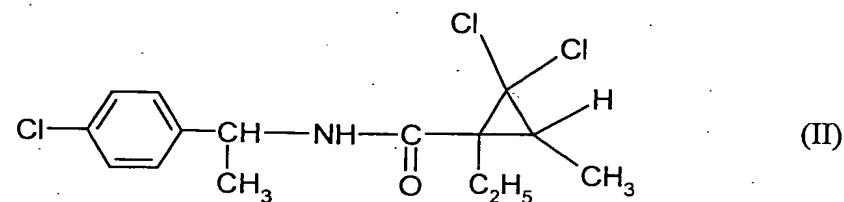
and

(1) N-[1-(4-chlorophenyl)ethyl]-2,2-dichloro-1-ethyl-3-methylcyclopropane-carboxamide of the formula

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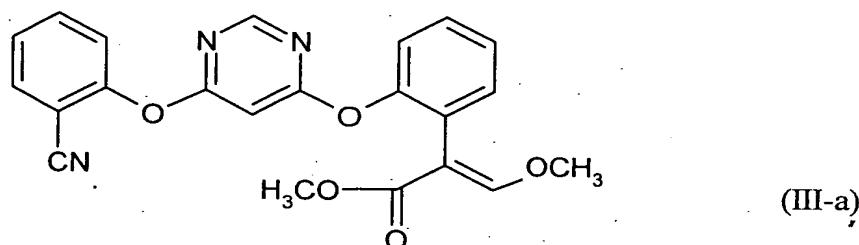
Donna J. Veach



and/or

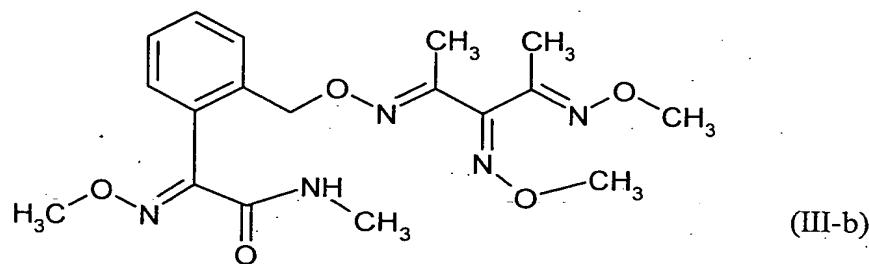
(2) a strobilurin derivative of the formula

5



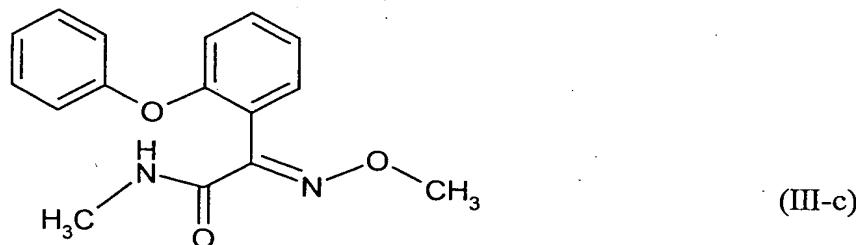
(azoxystrobin)

or



(orysastrobin)

or

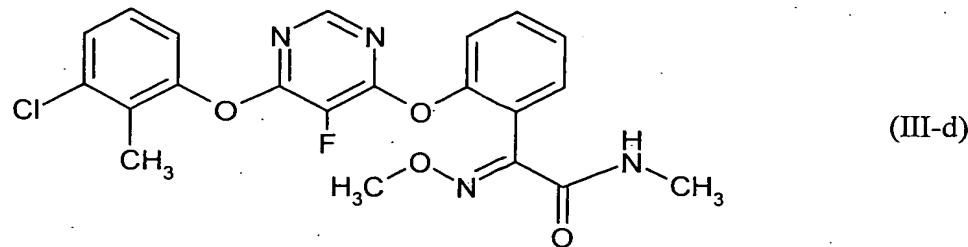


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(metominostrobin)

- 3 -

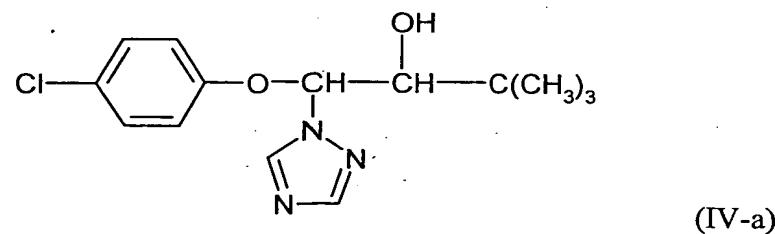
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and/or

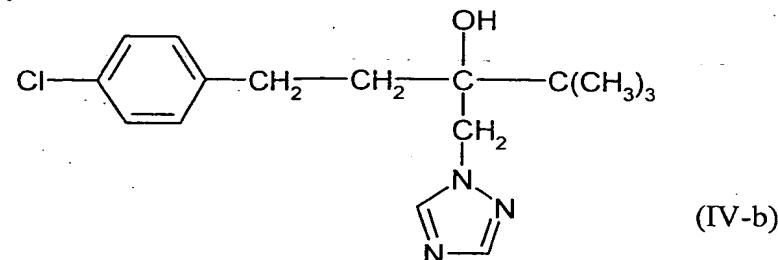
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(3) a triazole derivative of the formula



(triadimenol)

or

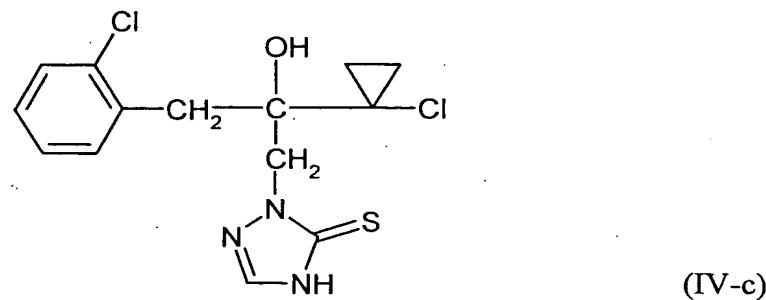


(tebuconazole)

10

or

- 4 -

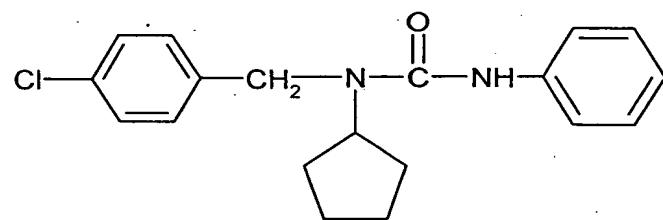


(prothioconazole)

and/or

(4) a phenylurea derivative of the formula

5



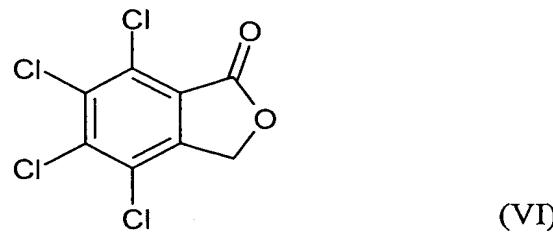
(V)

(pencycuron)

and/or

(5) the chlorophthalide of the formula

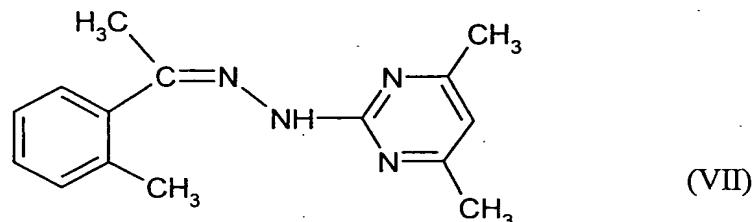
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(phthalide)

and/or

(6) the hydrazine derivative of the formula

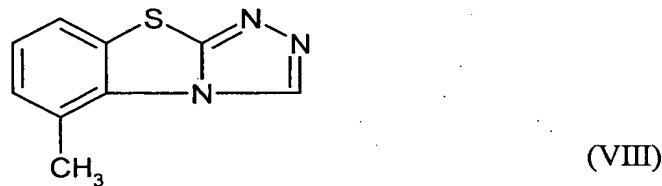


(ferimzone)

and/or

5

(7) the benzothiazole derivative of the formula

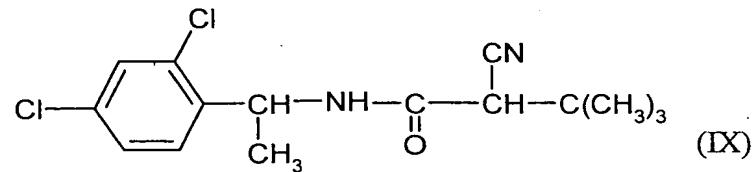


(tricyclazole)

and/or

10

(8) the cyanocarboxamide of the formula



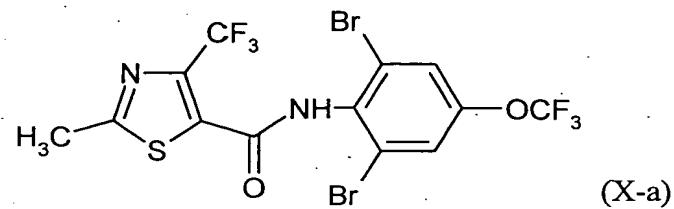
(diclocymet)

and/or

15

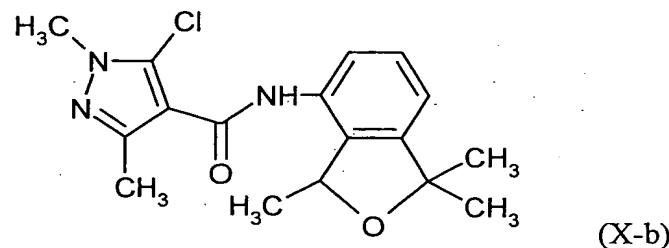
(9) a carboxamide derivative of the formula

- 6 -



(thifluzamide)

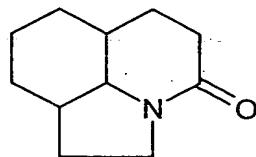
or



(furametpyr)

5 and/or

(10) the quinolone derivative of the formula

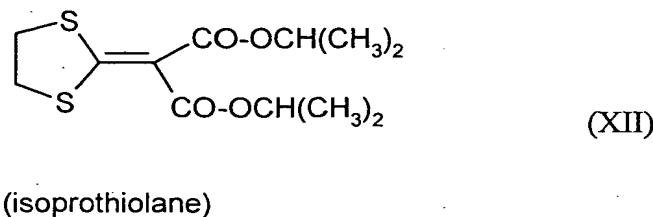


(XD)

(pyroquilon)

10 and/or

(11) the dithiolane derivative of the formula

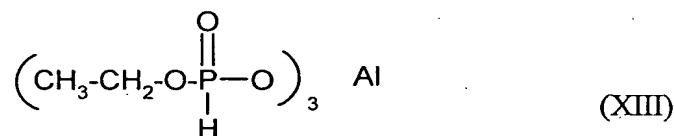


(isoprothiolane)

and/or

(12) the phosphorus compound of the formula

5

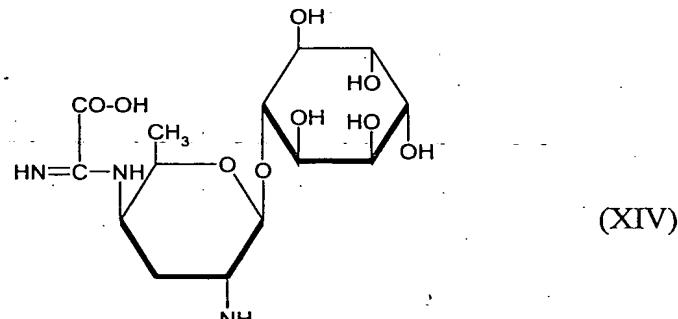


(fosethyl-Al)

and/or

(13) the iminoglycine derivative of the formula

10



(kasugamycin)

have very good fungicidal properties.

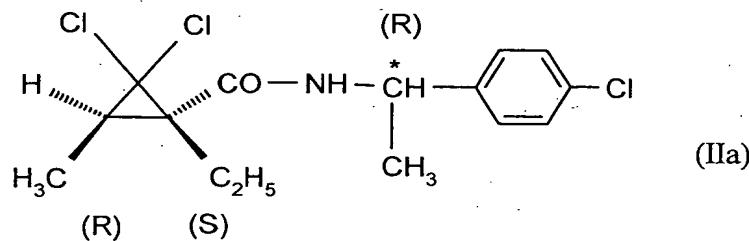
15 Surprisingly, the fungicidal activity of the active compound combinations according to the invention is considerably higher than the sum of the activities of the individual

active compounds. Thus, an unforeseeable, true synergistic effect is present, and not just an addition of activities.

2'-Cyano-3,4-dichloroisothiazole-5-carboxanilide of the formula (I) is known (cf. 5 WO 99-24 413).

From the structural formula of the active compound of the formula (II) it can be seen that the compound has three asymmetrically substituted carbon atoms. Accordingly, the product can be present as a mixture of different isomers or else in the form of a 10 single component. Particular preference is given to the compounds

N-(R)-[1-(4-chlorophenyl)ethyl]-(1S,3R)-2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxamide of the formula

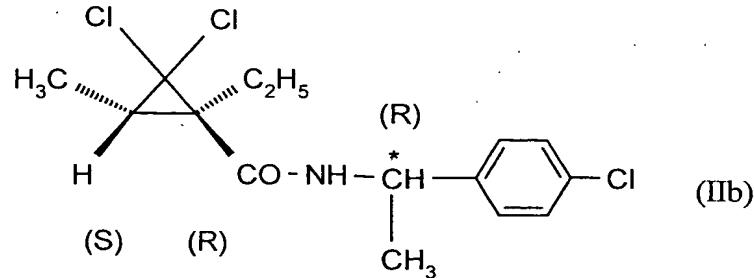


15

and

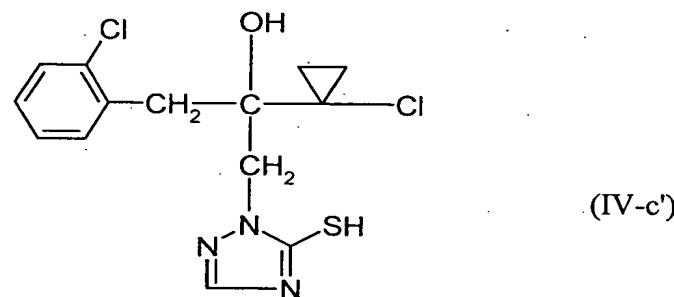
N-(R)-[1-(4-chlorophenyl)ethyl]-(1R,3S)-2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxamide of the formula

20



The mixture of the substances of the formulae (IIa) and (IIb) is known under the common name carpropamid.

5 Prothioconazole is mainly present in the "thiono" form of the formula (IV-c) given above. However, it can also be present in the tautomeric "mercapto" form of the formula



10 For the sake of simplicity, only the "thiono" form is shown in each case.

The compounds present in addition to the active compound of the formula (I) in the active compound combinations according to the invention are likewise known. Specifically, the active compounds are described in the following publications:

15

- (1) compounds of the formula (II) and individual isomers thereof  
EP-A 0 341 475

- (2) compounds of the formulae (III-a) to (III-d)

20

- EP-A 0 382 375  
DE-A 195 39 324  
EP-A 0 398 692  
WO 98-21 189

- 10 -

- (3) compounds of the formulae (IV-a) to (IV-c)

DE-A 2 324 010

EP-A 0 040 345

WO 96-16 048

5

- (4) compound of the formula (V)

DE-A 2 732 257

- (5) compound of the formula (VI)

10 Pesticide Manual, 9th Edition

(1991), page 801

- (6) compound of the formula (VII)

Pesticide Manual, 9th Edition

15 (1991), page 391

- (7) compound of the formula (VIII)

Pesticide Manual, 9th Edition

(1991), page 846

20

- (8) compound of the formula (IX)

JP-A 07-206 608

- (9) compounds of the formulae (X-a) and (X-b)

25 EP-A 0 371 950

EP-A 0 315 502

- (10) compound of the formula (XI)

Pesticide Manual, 9th Edition

30 (1991), page 746

(11) compound of the formula (XII)

Pesticide Manual, 9th Edition

(1991), page 506

5 (12) compound of the formula (XIII)

DE-A 2 456 627

(13) compound of the formula (XIV)

Pesticide Manual, 9th Edition

10 (1991), page 515

In addition to the active compound of the formula (I), the active compound combinations according to the invention comprise at least one active compound of the compounds of groups (1) to (13). In addition, they may also comprise further fungicidally or insecticidally active additives.

The synergistic effect is particularly pronounced when the active compounds in the active compound combinations according to the invention are present in certain weight ratios. However, the weight ratios of the active compounds in the active compound combinations can be varied within a relatively wide range. In general,

20 from 0.1 to 20 parts by weight, preferably from 0.2 to 10 parts by weight, of active compound of group (1),

25 from 0.1 to 20 parts by weight, preferably from 0.2 to 10 parts by weight, of active compound of group (2),

from 0.01 to 50 parts by weight, preferably from 0.02 to 20 parts by weight, of active compound of group (3),

- from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (4),
- 5       from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (5),
- from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (6),
- 10      from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (7),
- from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (8),
- 15      from 0.01 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (9),
- from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (10),
- 20      from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (11),
- 25      from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (12),
- from 0.1 to 100 parts by weight, preferably from 0.2 to 50 parts by weight, of active compound of group (13),
- 30      per part by weight of active compound of the formula (I).

The active compound combinations according to the invention have very good fungicidal properties and can be employed for controlling phytopathogenic fungi, such as Plasmodiophoromycetes, Oomycetes, Chytridiomycetes, Zygomycetes,  
5 Ascomycetes, Basidiomycetes, Deuteromycetes, etc.

The active compound combinations according to the invention are particularly suitable for controlling cereal and rice diseases, such as Pyricularia, Cochliobolus, Leptosphaeria, Rhizoctonia, Septoria, Pyrenophora, Pseudocercosporella, Erysiphe,  
10 Puccinia and Fusarium, and for controlling diseases encountered in viticulture, such as Uncinula, Plasmopara and Botrytis, and furthermore in dicotyledonous crops for controlling powdery and downy mildew fungi and causative organisms of leaf spot.

The fact that the active compound combinations are well tolerated by plants at the concentrations required for controlling plant diseases permits the treatment of above-ground parts of plants, of propagation stock and seeds, and of the soil. The active compound combinations according to the invention can be employed for foliar application or else as seed dressings.  
15

20 The active compound combinations according to the invention can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, microencapsulations in polymeric substances and into coating compositions for seed, and ULV formulations.

25 These formulations are produced in a known manner, for example by mixing the active compounds or active compound combinations with extenders, that is liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants, and/or foam formers. If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Suitable liquid solvents include, essentially: aromatics such as xylene, toluene  
30 or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such

as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water. Liquefied gaseous extenders or carriers are to be understood as meaning liquids which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants such as butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates. Suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks. Suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, or else protein hydrolysates. Suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose, and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian blue, and organic dyestuffs such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95% by weight of active compounds, preferably between 0.5 and 90%.

In the formulations, the active compound combinations according to the invention can  
5 be present as a mixture with other known active compounds such as fungicides,  
insecticides, acaricides and herbicides, and as mixtures with fertilizers or plant growth  
regulators.

The active compound combinations can be used as such, in the form of their  
10 formulations or as the use forms prepared therefrom, such as ready-to-use solutions,  
emulsifiable concentrates, emulsions, suspensions, wettable powders, soluble powders  
and granules. They are used in the customary manner, for example by watering,  
spraying, atomizing, scattering, spreading, and as a powder for dry seed treatment, a  
solution for seed treatment, a water-soluble powder for seed treatment, a water-soluble  
15 powder for slurry treatment, or by encrusting.

When using the active compound combinations according to the invention, the  
application rates can be varied within a relatively wide range, depending on the kind of  
application. In the treatment of parts of plants, the application rates of active compound  
20 combination are generally between 0.1 and 10,000 g/ha, preferably between 10 and  
1000 g/ha. In the treatment of seed, the application rates of active compound  
combination are generally between 0.001 and 50 g per kilogram of seed, preferably  
between 0.01 and 10 g per kilogram of seed. In the treatment of the soil, the application  
rates of active compound combination are generally between 0.1 and 10,000 g/ha,  
25 preferably between 1 and 5000 g/ha.

The good fungicidal activity of the active compound combinations according to the  
invention is evident from the examples below. While the individual active compounds  
exhibit weaknesses with regard to the fungicidal activity, the combinations have an  
30 activity which exceeds a simple addition of activities.

A synergistic effect of fungicides is always present when the fungicidal activity of the active compound combinations exceeds the total of the activities of the active compounds when applied individually.

- 5      The expected activity for a given combination of two active compounds can be calculated according to S.R. Colby ("Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", Weeds 15, (1967), 20-22) as follows:

If

10     X      is the efficacy when applying active compound A at an application rate of m g/ha,

15     Y      is the efficacy when applying active compound B at an application rate of n g/ha, and

E      is the efficacy when applying the active compounds A and B at application rates of m and n g/ha,

20     then

$$E = X + Y - \frac{X \cdot Y}{100}$$

The efficacy is calculated in %. 0% is an efficacy which corresponds to that of the control, while an efficacy of 100% means that no infection is observed.

25     If the actual fungicidal activity exceeds the calculated value, then the activity of the combination is superadditive, i.e. a synergistic effect exists. In this case, the efficacy which was actually observed must be greater than the value for the expected efficacy (E) calculated from the abovementioned formula.

30     The examples that follow illustrate the invention.

Examples

Example 1

5 Erysiphe test (barley)/protective

Solvent: 50 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound or a combination of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

15

To test for protective activity, young plants are sprayed with the preparation of active compound at the stated application rate.

1 day after the treatment, the plants are dusted with spores of *Erysiphe graminis* f.sp.

20 hordei.

The plants are placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of mildew pustules.

25 Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

30

**Table 1**

Erysiphe test (barley)/protective

Active compound	Active compound application rate in g/ha	Efficacy in %
<u>Known:</u>    (I)	100 50	0 0
<u>Known:</u>    (V)	50	0
<u>According to the invention:</u>  (1) + (V)  1:1	50 + 50	calc.*    found 0            26

\* Calculated using Colby's formula

**Example 2**

Pyricularia test (rice)/protective

5 Solvent: 50 parts by weight of dimethylformamide  
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound or a combination of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

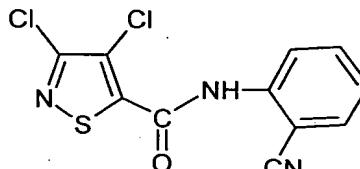
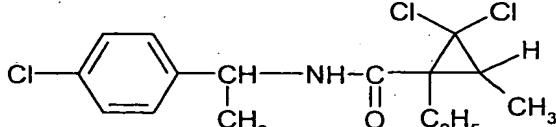
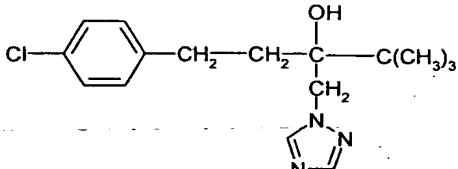
15 To test for protective activity, young rice plants are sprayed with the preparation of active compound at the stated application rate. 1 day after the treatment, the plants are inoculated with an aqueous spore suspension of Pyricularia oryzae. The plants are then placed in a greenhouse at 100% relative atmospheric humidity and 25°C.

20 Evaluation is carried out 4 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

**Table 2**

Pyricularia test (rice)/protective

Active compound	Active compound application rate in g/ha	Efficacy in %
<u>Known:</u>   (I)	100 50	0 0
<u>Known:</u>   (II)	50	29
<u>Known:</u>   (IV-b)	100	0

**Table 2** (continued)

Active compound	Active compound application rate in g/ha	Efficacy in %
<u>Known:</u>		
 (IV-c)	100	29
<u>According to the invention:</u>		calc.* found
$\begin{array}{c} (\text{I}) \\ + \\ (\text{II}) \end{array} \quad \left\{ \quad \begin{array}{c} 50 \\ + \\ 50 \end{array} \right\}$ 1:1	29	50
$\begin{array}{c} (\text{I}) \\ + \\ (\text{IV-b}) \end{array} \quad \left\{ \quad \begin{array}{c} 100 \\ + \\ 100 \end{array} \right\}$ 1:1	0	36
$\begin{array}{c} (\text{I}) \\ + \\ (\text{IV-c}) \end{array} \quad \left\{ \quad \begin{array}{c} 100 \\ + \\ 100 \end{array} \right\}$ 1:1	29	57

\* Calculated using Colby's formula